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Low Frequency Sound Absorption in Sea Water: A New Chemical Relaxation Mechanism?

A Paper Presented at the 101st Meeting of the Acoustical Society of America, 18-22 May 1981 Ottawa, Canada

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Preface

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Reviewed and Approved: 1 September 1981

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This document presented the oral and visual presentation entitled "Low Frequency Sound Absorption in Sea Water: A New Chemical Relaxation Mechanism?," presented at the 101st Meeting of the Acoustical Society of America, 18-22 May 1981, in Ottawa, Ontario, Canada.

Excess sound absorption in sea water arises mainly from chemical relaxations involving $MgSO_4$ and $B(OH)_3$. The high-frequency (100 kHz) $MgSO_4$ relaxation has been identified as a multistep ion-pair process. The low frequency

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(1 kHz) and $B(OH)_3$ relaxation apparently involves more complex interactions with other constituents. To investigate $B(OH)_3$ interactions in a simpler system, we measured absorption in NH_3 solution using the resonator method. We have found α_{max} to be proportional to the product of $NH_4^{(+)}$ and $B(OH)_4^{(-)}$ concentrations; however, the magnitude is much too large to be caused by the ion pair. The mechanism, probably similar to that in sea water, resembles catalysis, the absorption being governed by the large volume change of the faster NH_3/NH_4^+ equilibrium and the relaxation frequency by the slower $B(OH)_3/B(OH)_4^-$ equilibrium.

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Low-Frequency Sound Absorption in Sea Water:
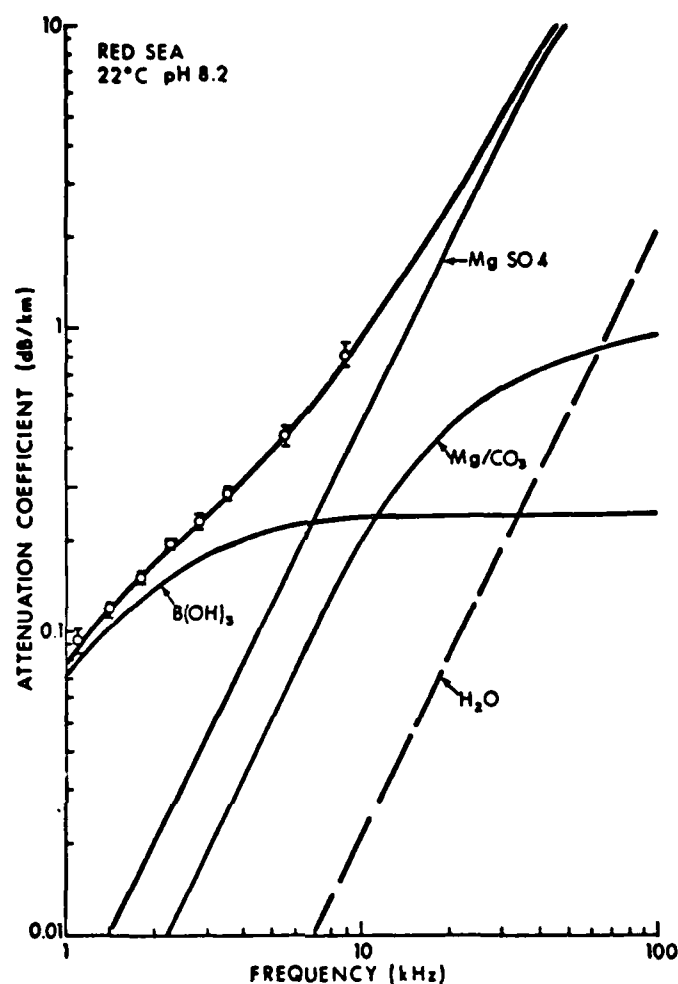## A New Chemical Relaxation Mechanism?
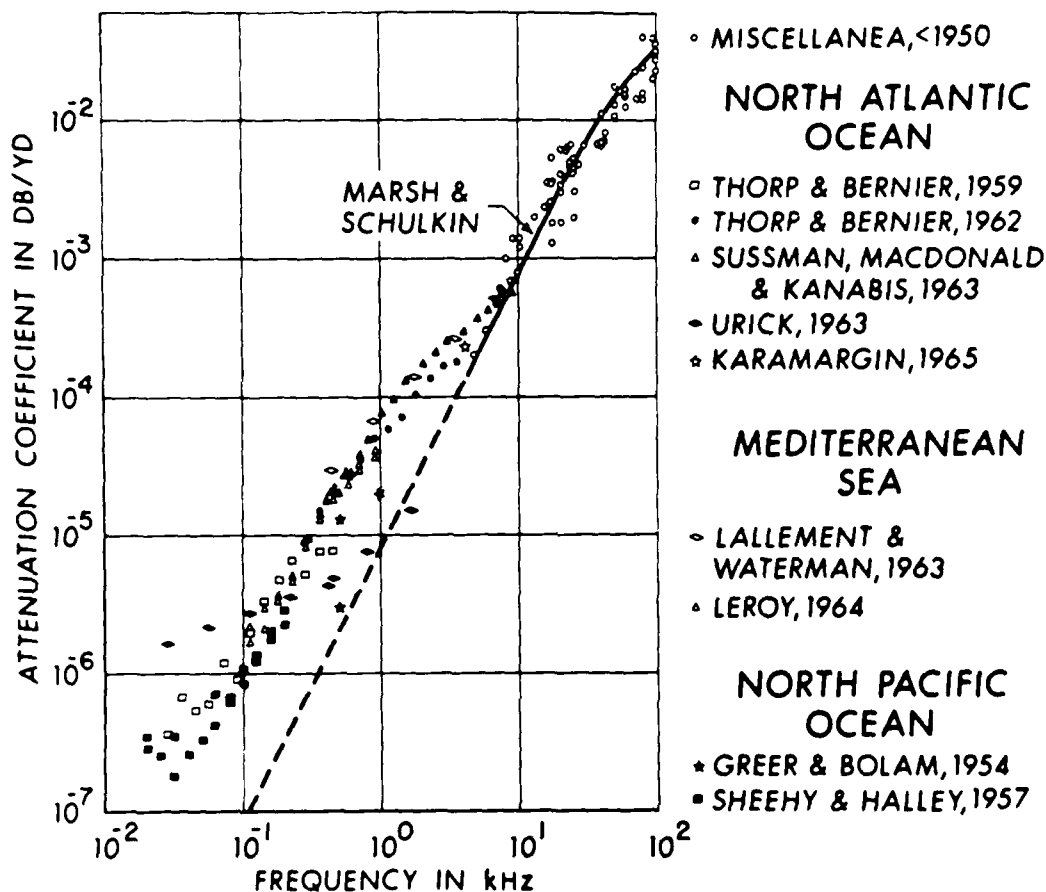
Slide 1

Since the publication in 1965 of a summary paper by Bill Thorp of NUSC, which showed the attenuation of low frequency sound in sea water to be anomalously high, the subject has received much attention, especially during the last decade.

It has been shown that this attenuation is due to absorption by a chemical relaxation reaction. Yeager and Fisher first identified boron as an essential component in the reaction.

This paper will review what we know — and don't know — about this low-frequency absorption based on our recent resonator measurements.

Slide 2

To put this absorption in perspective, it is one of three chemical relaxation mechanisms that are responsible for sound attenuation in sea water. The resultant of these three components (the outside solid line) is in excellent agreement with at-sea measurements, in this case our measurements in the Red Sea.

At high freqeuncies a magnesium-sulphate reaction dominates; at mid-frequencies there is a significant, but not dominant magnesium carbonate reaction; and at low frequencies the boric acid relaxation, which we are interested in, dominates.
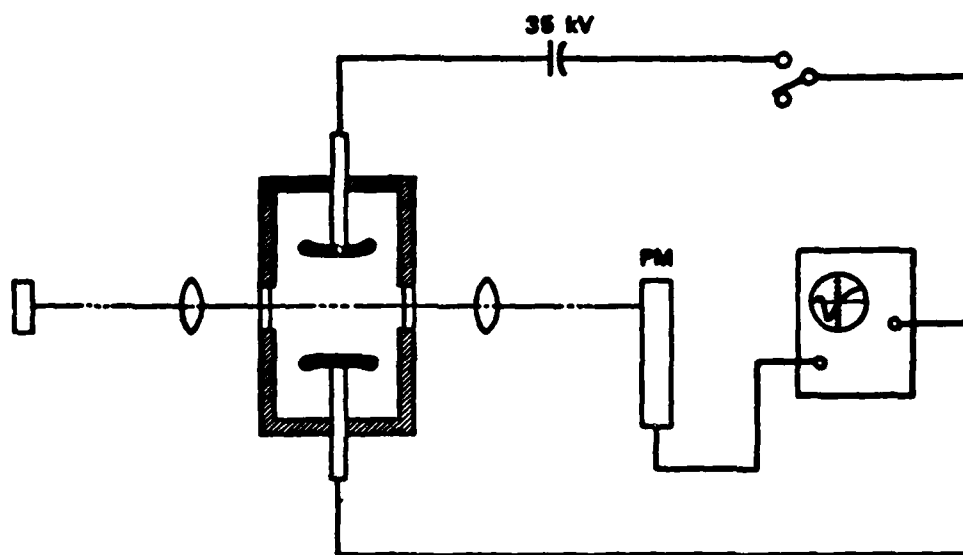
TEMPERATURE-JUMP APPARATUS

Slide 3

Laboratory measurements of the low frequency relaxation were first conducted in Dr. Yeager's laboratory using the temperature-jump technique (or T-jump technique) and were continued at Scripps by Fisher and Simmons. (CAPT Vern Simmons was later a Program Officer at NUSC.)

The T-jump technique determines the relaxation frequency of a reaction, but not the magnitude of the corresponding absorption that will turn out to be significant.

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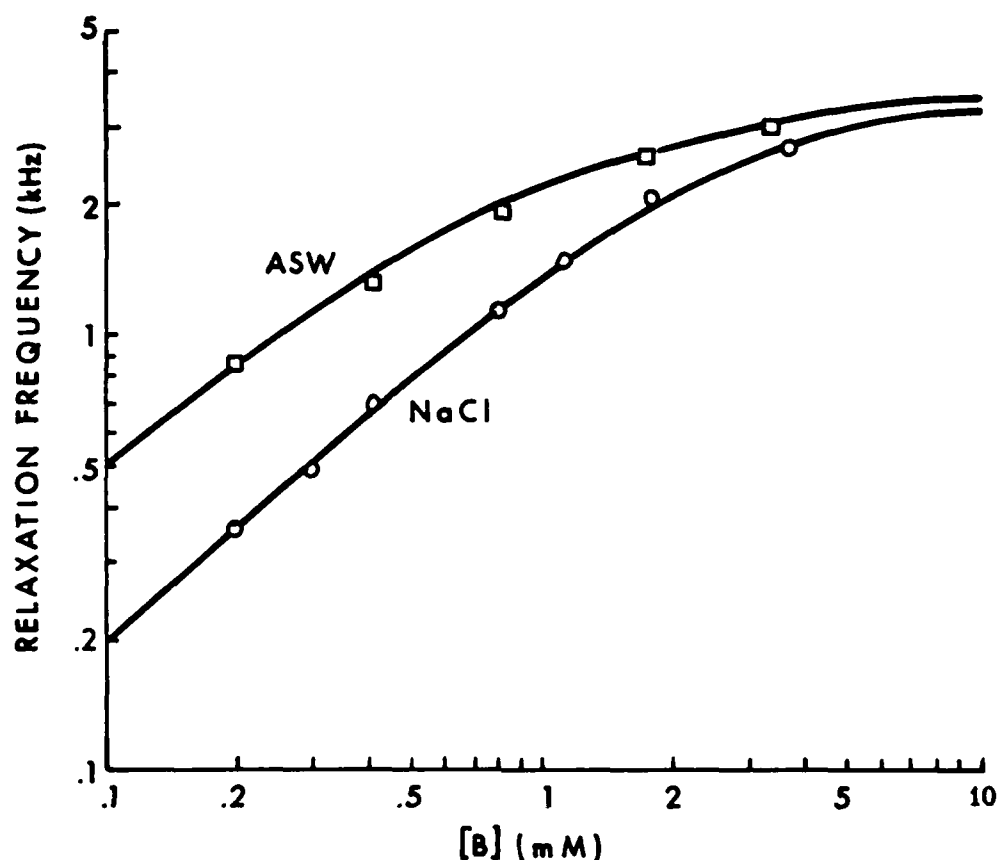
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By systemically adding or omitting the constituents of artificial sea water (abbreviated as ASW — not the ASW most of you are familiar with), Yearger and Fisher showed that boron was essential to the reaction. The relaxation frequency was in good agreement with that obtained from our at-sea measurements.

Simmons obtained the relaxation frequency as a function of Boron concentration in artificial sea water, reaching an asymtotic value of 3.5 kilohertz. For the naturally occurring boron concentration in sea water (0.5 millimoles), the relaxation frequency is 1.5 kilohertz, as expected, for room temperature.

When Simmons repeated the same experiment with only sodium chloride added to the boron, the relaxation frequency was, somewhat surprisingly, consistently lower. This implied that there could perhaps be different interactions with the boron in each case.

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_3 \cdot OH^- \rightleftharpoons B(OH)_4^-$$
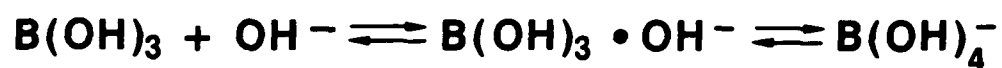
TWO STEP REACTION

Slide 5

Based on the asymptotic behavior of the relaxation frequency in artificial sea water, Simmons proposed a two-step boron/boric acid reaction to explain the low frequency absorption. It is the second step, on the right, that is the slow reaction that causes the absorption of sound.
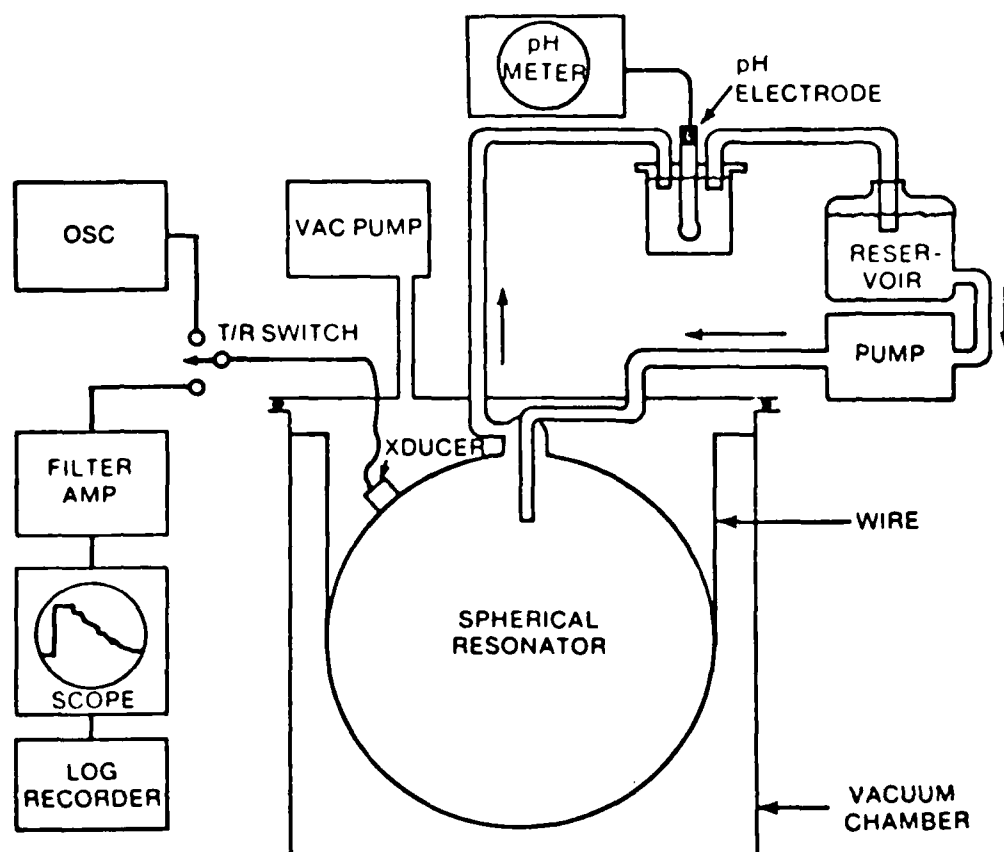
Slide 6

To directly measure the absorption of low frequency sound in the laboratory, the resonator technique is used. In practice, due to size and weight restrictions, very low frequency measurements are difficult, but this can be compensated for by increasing the concentration and temperature over normal sea water conditions. These results can then be extrapolated back to normal sea water conditions.

Our system had a 72-liter resonating sphere that gave good results down to 10 kilohertz. We developed a direct supply and pH monitoring system to facilitate these measurements and this technique is now being used by other investigators.
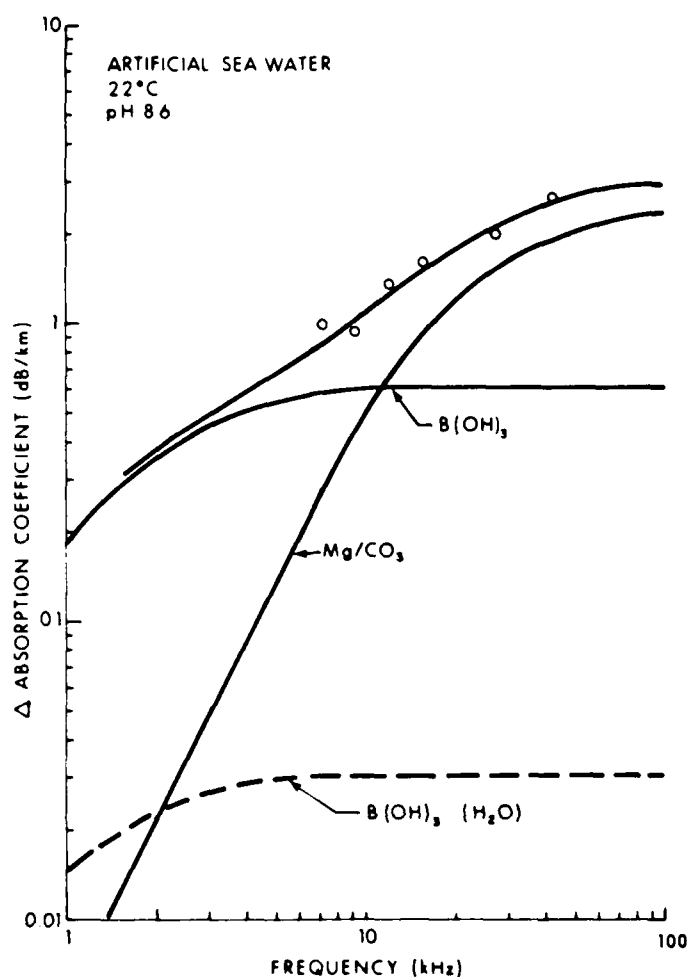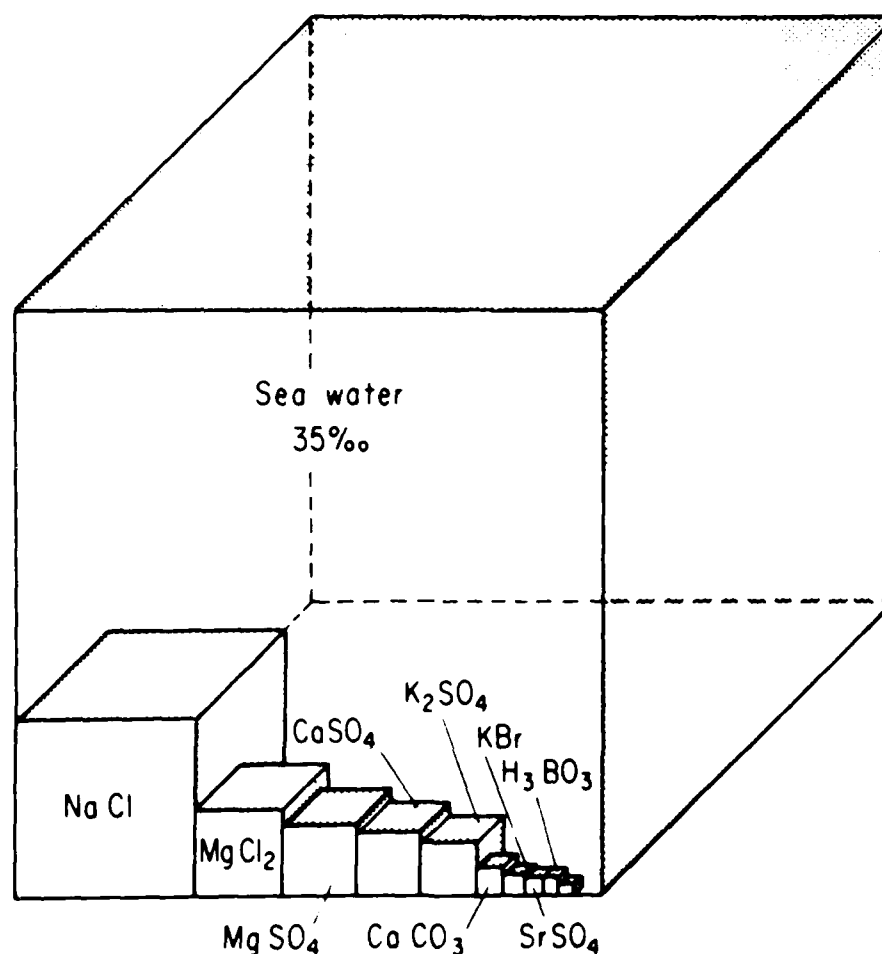
Slide 7

The absorption obtained from the resonator measurements provided both a verification and a surprise. For artificial sea water, the observed absorption is as expected from at-sea data and the corresponding relaxation frequency agrees with the T-jump measurements. Everything is fine.

However, the boric acid alone (shown by the dashed line down at the bottom of the figure) had an absorption that was much less than artificial sea water.

The logical explanation is that another constituent of sea water acts to enhance the boron absorption.

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The key question then is what constituent, or constituents, could be responsible. Fortunately, the possibilities are not endless, as this standard diagram of the sea water constituents shows. The concentrations drop off rapidly, so that you can ignore many trace components.

We have found that two other constituents, Ca and CO_2, were required to enhance the boron absorption to the level observed in sea water.
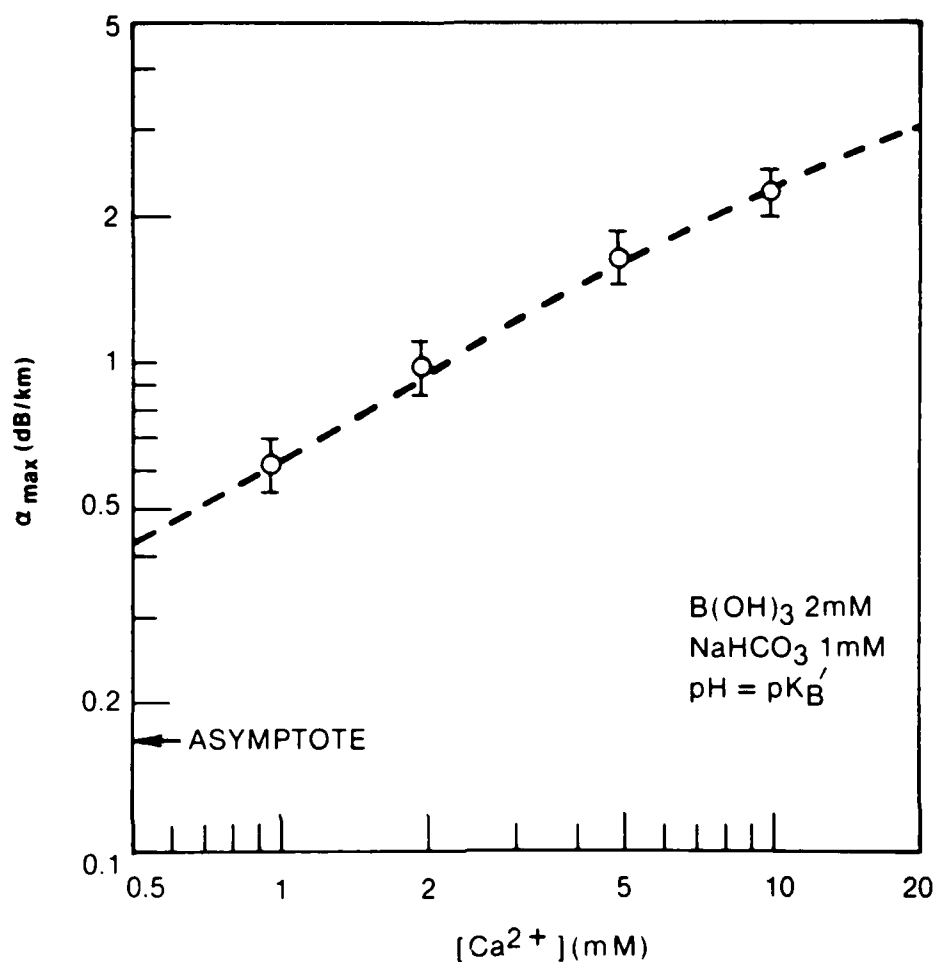
Slide 9

The effect of each of these two additional components was observed to be different. For example, the effect of CO_2 did not depend strongly on concentration. The effect of Ca, on the other hand, was concentration-dependent, as shown here.

For the range of concentration shown (0.5 to 20 millimoles), there is an order of magnitude change in absorption. At the bottom left, we have indicated the asymptotic value (0.18) that is obtained at near zero concentrations.
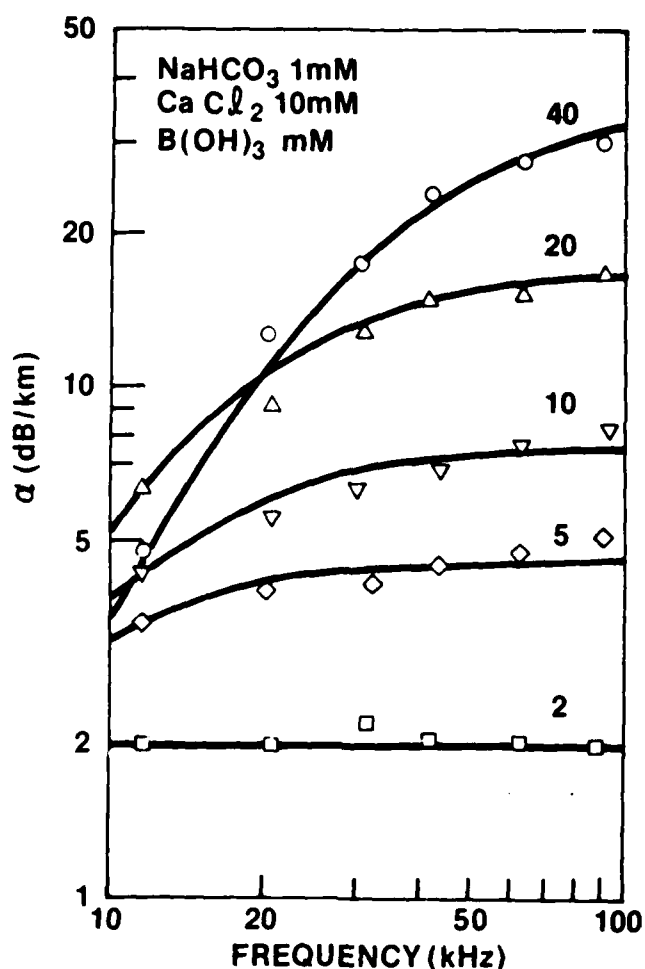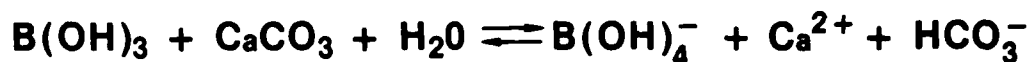
Slide 10

When we increase the boron concentration (shown on the right for each curve) while holding the other two components constant, there is a corresponding rise in absorption.

The behavior of the relaxation frequencies is very interesting. At the lowest boron concentration (2 millimoles), we are clearly in the asymptotic region of a relaxation frequency probably not far from the 3.5 kilohertz reported by Simmons. However, as we increase the concentration, the relaxation frequency shifts upwards, reaching approximately 30 kilohertz for the 40 millimole boron concentration.

We are now with a dilemma: the boron/boric acid reaction alone has the observed relaxation frequency, but not a sufficient absorption. Adding Ca and CO_2 brings the absorption up to the proper value, but we are faced with a concentration dependent relaxation frequency greatly exceeding 3.5 kilohertz at higher concentrations.

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$$B(OH)_3 + CaCO_3 + H_2O \rightleftharpoons B(OH)_4^- + Ca^{2+} + HCO_3^-$$

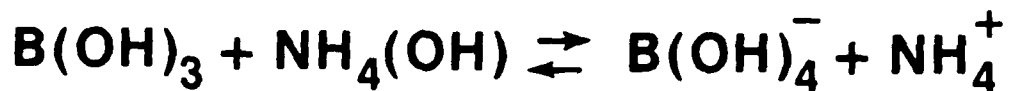## PROPOSED EXCHANGE REACTION

Slide 11

The only way that we could explain this behavior was to propose an exchange reaction between the boron/boric acid system and a carbonic acid/CO_2 system.

This is in line with the general exchange reaction proposed by Yeager in the original article on the boron absorption in 1973. It is difficult to see, however, how the second constituent, calcium, fits into the picture. At higher concentrations, we believe that the non-relaxing part of this reaction dominates so that the T-jump measurements simply do not see the higher relaxation frequencies. This would explain the asymptotic 3.5 kilohertz value measured by Simmons in artificial sea water.
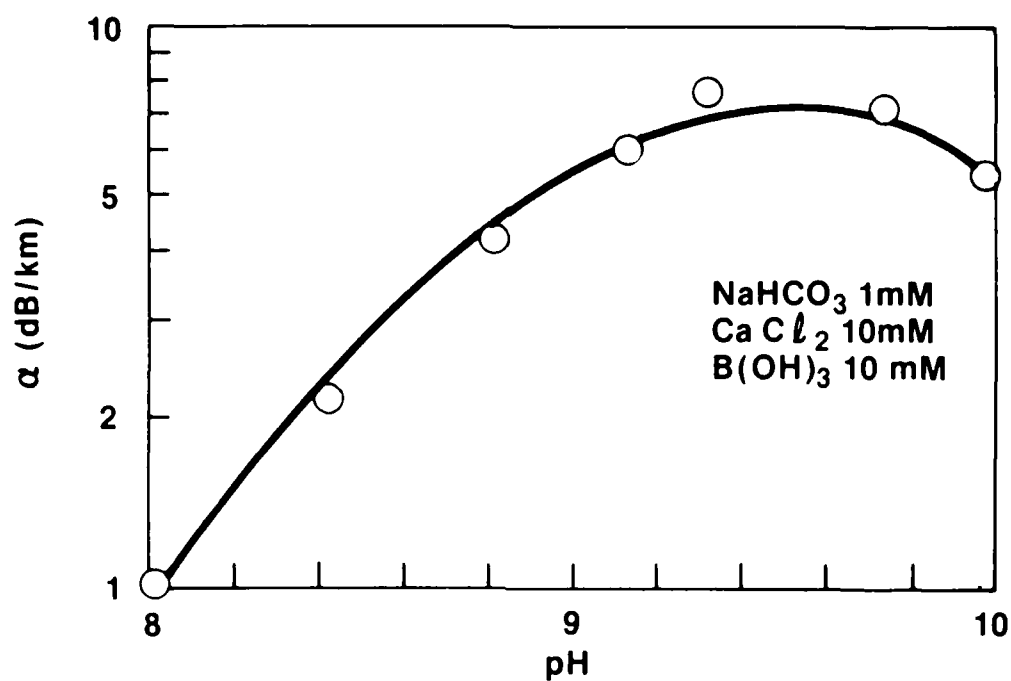
Slide 12

The measured pH dependency of absorption agrees with that predicted for such an exchange reaction, reaching a maximum value at pH = 9.5. So we have additional evidence for an exchange reaction.

$$B(OH)_3 + NH_4(OH) \rightleftharpoons B(OH)_4^- + NH_4^+$$

YEAGER HYPOTHESIS (1973)

$$B(OH)_3 + L + H_2O \rightleftharpoons B(OH)_4^- + (HL)^+$$
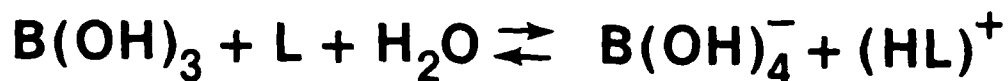
Slide 13

If a boron exchange reaction is the key to the low frequency absorption, we could ask: "Are there other substances that would react with boron in the general way proposed by Yeager in 1973 for a Lewis base?" Yeager's general form is shown on the bottom line with the Lewis base designated by L.

A likely candidate might be ammonia, which should have the straightforward reaction shown in the top line.
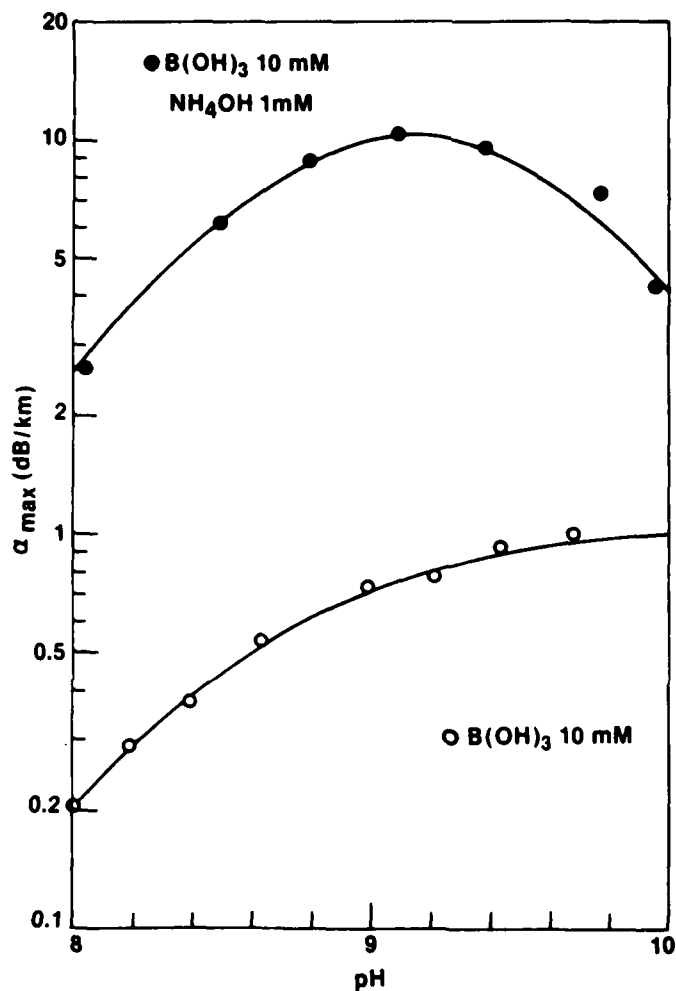
Slide 14

This is indeed the case, observe the change in absorption obtained by the addition of 1 millimole of ammonium hydroxide to 10 millimoles of boric acid. Note also the characteristic pH dependence for an exchange reaction when the ammonium hydroxide is added.

There are several implications. First, this reaction might be responsible for the additional excess absorption observed in sea water below 100 hertz. Secondly, it is possible to enhance the absorption due to the low frequency boron reaction.

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CONCLUSIONS

1. Other ions involved in low frequency boron relaxation.

2. Data suggest an exchange reaction.

3. Enhancement of absorption possible.

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We can summarize our results with three conclusions:

1. Two other sea water constituents, Ca and CO_2, are involved in the low frequency boron absorption.

2. The data support an exchange reaction as the principal mechanism, but the essential role of Ca is not fully understood.

3. Enhancement of the low frequency absorption is possible.

Thank you.

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